

# **Growth and Characterization of III-V Semiconductors for Device Applications**

**Final Report**

submitted by

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## **Project Summary**

The research goal was to achieve a fundamental understanding of the physical processes occurring at the surfaces and interfaces of epitaxially grown InGaAs/GaAs (100) heterostructures. This will facilitate the development of quantum well devices for infrared optical applications and provide quantitative descriptions of key phenomena which impact their performance. Devices impacted include high-speed laser diodes and modulators for fiber optic communications at 1.55  $\mu\text{m}$  wavelengths and intersub-band lasers for longer infrared wavelengths. The phenomenon of interest studied was the migration of indium in InGaAs structures. This work centered on the molecular beam epitaxy reactor and characterization apparatus donated to CAU by AT&T Bell Laboratories. The material characterization tool employed was secondary ion mass spectrometry. The training of graduate and undergraduate students was an integral part of this program. The graduate students received a thorough exposure to state-of-the-art techniques and equipment for semiconductor materials analysis as part of the Master's degree requirement in physics. The undergraduates were exposed to a minority scientist who has an excellent track record in this area. They also had the opportunity to explore surface physics as a career option. The results of the scientific work was published in a refereed journal and several talks were presented professional conferences and academic seminars.

### **1 Project Description**

Molecular beam epitaxy (MBE), chemical beam epitaxy (CBE) and metal-organic chemical vapor deposition (MOCVD) are non-equilibrium growth processes that allow the growth of pseudomorphic overlayers onto dissimilar substrates with which the overlayer may be mismatched by several percent. Lattice mismatched III-V heterojunctions have many potential optoelectronic applications. An important aspect of the growth of these heterojunctions is the quality of the interface. A non-abrupt interface and/or the diffusion of constituents across the interface contributes directly to alloy scattering, a loss mechanism in devices that depend on charge transport, and modification of potential profiles in quantum well structures. In As-based structures, it is also known that changes in the column III element to As ratio can alter the reconstruction at the surface of the growth with profound consequences for the electronic structure of the material.

A primary area of concern in quality control is the long term stability of electronic properties based on material parameters, i. e., aging effects. Typical failure modes for semiconductor lasers, for example, are spectral instabilities such as wavelength shifts and temporal increases in the operating current needed to maintain constant optical output. The epitaxial growth of InGaAs based systems is characterized by the segregation of In at the growth front and at interfaces with other arsenides, particularly those with higher heats of formation (e. g., Ga and Al) and smaller covalent radii. This segregation results in poor composition profiles and poor interfacial width control. It has been demonstrated that the efficiency of wavelength tuning of InGaAsP distributed-Bragg-reflector lasers by current injection decreases substantially with accelerated aging. This may, from a materials perspective, be due to the segregation of In to the interface with current injection. The

result is the alteration of the potential energy profiles of the active layer quantum wells. Transport devices such as modulation doped field effect transistors are also adversely affected by changes in the In segregation. The obvious effect is a change in the emitter to base or/and base to collector capacitance(s) (or bias voltage(s)). Additionally, the segregation results in a change in the alloy concentrations at the interfaces and surfaces of the device. The consequence of this latter phenomenon in transport devices is the modification of the density of scattering centers, i. e., alloy scattering effects on the mobility of the charge carriers. The effects of In segregation on the electronic structure and stoichiometry in the devices described above are significant. The ability to adequately control the In segregation will lead to a significant improvement in quality without changes in the device fabrication process.

The area of interest for this investigation was the segregation of In at the growth front of InGaAs (100) grown by MBE and its effects on the valence band structure using *in situ* reflection high energy electron diffraction (RHEED), ultraviolet photoemission spectroscopy (UPS) and secondary ion mass spectrometry (SIMS) under various growth conditions. The *in situ* electronic structure analysis portion of the project was not achievable due to a significant hardware failure and a long recovery period. SIMS analysis of procured samples grown by various techniques under various conditions enabled the analysis of factors controlling the incorporation of In into the InGaAs lattice. The growth kinetics of the materials grown by the different epitaxial techniques were analyzed and compared. An attempt was made to provide a diagnostic analog for MOCVD growth based upon this comparison. The work has been documented in the scientific literature and through technical presentations.

## 2 Objectives

The work involved here was concerned with obtaining a fundamental understanding of the nature of the mechanisms responsible for the segregation of In from the InGaAs/GaAs interface and its effect on the electronic band structure of the material. SIMS was used for the analysis of the growth kinetics and *in situ* UPS was to be used to monitor the electronic structure. The approach used here is also extendable to other relevant material systems. The achieved objective was to study the reaction kinetics of the In segregation with respect to the In stoichiometry and epitaxial growth technique.

## 3 Accomplishments

### 3.1 Infrastructure

A considerable portion of the project's efforts was spent on the installation of the materials growth and analysis systems and related sub-systems. The relevant items of interest for this project are a Riber model 2300 solid source MBE reactor for the growth of III-V (arsenides) material, a secondary ion mass spectrometer (60 Å depth resolution with Atomika O<sub>2</sub><sup>+</sup> source) for depth profiling, a custom Perkin Elmer surface analysis system for Auger and photoemission spectroscopies equipped with a VSW UV-10 ultraviolet discharge lamp and a VSW twin anode (Y and Mg) x-ray source, a Philips 501B scanning electron microscope (100 Å resolution), and miscellaneous vacuum hardware. The SIMS and photoemission systems were installed and commissioned for operation. A considerable amount of this capital equipment was donated by AT&T Bell

Laboratories (now Lucent Technologies) to facilitate the development of this work. CAU provided a Polycold Systems model PFC 100 cryogenic heat exchanger and a Neslab HX 300A recirculating chiller to support the MBE reactor, a Terra Universal Series 100 nitrogen glove box for MBE sample preparation, a Balston 75-92 ultra high purity nitrogen generator for environmental control and purging, a Barnstead E-pure DI water still for wafer processing, and laboratory space with facilities support. The cryogenic heat exchanger, the electron microscope, and the photon sources for the photoemission spectroscopy require a chilled water supply for their operation. A closed loop chilled water system was designed for this purpose and installed using the Neslab recirculating chiller.

### **3.2 Methodology and Procedures**

The epitaxial material was to be grown by conventional solid source MBE in the Riber growth system under As<sub>4</sub> stabilized conditions. The *in situ* aspect of the UPS analysis was accomplished by connecting the UPS analysis chamber to the growth system with an intermediate load lock vessel such that ultra-high vacuum conditions were maintained. An ultra high vacuum load lock chamber was constructed from existing and purchased components. It was coupled between the reactor and the existing UPS analysis chamber. The chambers were isolated from each other with metal sealed gate valves. The unique aspect of this coupling of the MBE growth with the density of state analysis provided by UPS is that it allows the electronic evolution of a device structure to be monitored as the device is grown in sequential steps. Samples were to be loaded into the system through the load lock. The load lock was equipped with heaters for outgassing of samples prior to

insertion into the MBE or UPS chambers. This load lock can accommodate up to four mounted samples thus minimizing downtime.

The samples and substrates used in the MBE and surface analysis systems require chemical processing to remove contamination and controlled environments to maintain their integrity after preparation. A Labconco fume hood was purchased and installed in the laboratory for chemical processing. The fume hood had an access port cut out of its side for insertion of a pass through load lock. This load lock was attached to the Terra Universal glove box. The glove box is purged with high purity nitrogen. The nitrogen is generated by the Balston ultra high purity nitrogen generator and delivered through a stainless steel manifold which was designed and installed for this purpose. Samples are chemically processed in the fume hood and passed through to the glove box for mounting onto holders. The mounted samples can then be loaded with minimal exposure to the atmosphere into the vacuum load lock of the combined MBE/UPS system.

The MBE reactor underwent an extensive bake-out under vacuum conditions to remove residual water vapor from the system. The effusion cells for the elemental charges used in the epitaxial growth process were subsequently baked-out in the reactor again under vacuum conditions. The cells were removed and loaded with the appropriate charges and reinserted into the reactor for outgassing and growth rate calibration. The reactor's liquid nitrogen heat transfer shroud, used to maintain a low background pressure during the growth process, was modified with fittings to accommodate the use of the Polycold closed cycle cryogenic heat exchanger. The motivation for this arrangement was that the closed cycle design promised to be more cost effective than that of the typical

flow through configuration using liquid nitrogen. Two of our industrial partners (TLC Precision Wafer Manufacturing and Lasertron) are interested in evaluating this modification for their own use as liquid nitrogen is a major consumable item.

The MBE reactor, unfortunately, suffered extensive damage during installation of the closed cycle cryogenic refrigerator. The LN<sub>2</sub> heat transfer shrouds in the reactor were incompatible with the high pressure operation of the refrigerator. Parts were scavenged from the other Riber MBE system in the lab and the system was made operational for GaAs growth (cells loaded and outgassed) using conventional liquid nitrogen cooling. The university's insurance carrier settled the claim for the damage after several months and replacement parts were ordered. TLC Precision Wafer Manufacturing, our industrial partner, provided extensive help in getting the system back to operational status.

### **3.3 Research**

In light of the aforementioned mishap, the SIMS analysis of the ternary InGaAs material was moved up in priority over the *in situ* UPS and RHEED measurements. Multilayer samples of MBE grown In<sub>0.53</sub>Ga<sub>0.47</sub>As where each individual layer was grown at a different substrate temperature were obtained from a collaboration with Theda Daniels-Race of the Electrical and Computer Engineering Dept. at Duke University. This sample in conjunction with samples of CBE and MOCVD grown InGaAs acquired from Lucent Technologies - Bell Laboratories formed the basis for a comparative analysis of the similarities of the growth techniques. MOCVD and CBE both use the same metal-organic precursors for the deposition of the elemental species. There are however, pronounced differences in the techniques. The first is in the operating pressure regimes. MOCVD can

be characterized as a low (~ 10 Torr) to atmospheric pressure technique. Unfortunately, as a result, very little in the way of process monitoring has been available. Process control has until recently been achieved by *ex situ* analysis of the grown material. *In situ* x-ray diffraction and optical reflectance/ spectroscopic monitoring by have been demonstrated but are limited typically by geometric and mechanical constraints of the typical system. In contrast to the MOCVD process, the CBE process is facilitated with a vacuum of  $\sim 10^{-6}$  Torr. It is thus amenable to *in situ* surface sensitive electron and ion spectroscopies for characterizing the growth. In addition to the obvious difference in the operational pressures as stated above, these processes differ fundamentally in their deposition kinetics. In CBE, the pyrolysis of the precursors occurs on the surface of the heated substrate. The volatile species then desorb and leave behind the elemental species which subsequently chemisorb onto preferred sites. The analysis and modeling of this process has received much attention in the literature. In MOCVD, the pyrolysis of the precursors occurs mostly in the gas phase with the balance occurring after the constituents diffuse through a stagnant boundary layer to the substrate. In the typical MOCVD configuration, both the substrate and the precursors are radiantly heated from below by infrared sources external to the growth reactor.

The kinetics of the growth of  $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$  grown by MOCVD and CBE were examined and compared. This material is lattice matched to InP (100) and is commonly used both as a buffer layer prior to growing device structures and as a barrier layer in InGaAs/InP multiple quantum well devices. The material grown by MBE was also examined and was used as a point of reference. SIMS proved to be an excellent technique to characterize the growth stability and the incorporation of the column III constituents,

with respect to the substrate temperature,  $T_s$ . The kinetics were measured specifically by following the Ga/In ratio versus  $T_s$ . The samples are multilayer structures where each layer was grown at a different  $T_s$ . The immediate focus was to provide a diagnostic analog for the MOCVD grown material. The manuscript documenting this analysis was submitted and accepted for publication ("Comparison of InGaAs (100) Grown by Chemical Beam Epitaxy and Metal Organic Chemical Vapor Deposition", M. D. Williams, A. L. Greene, T. Daniels-Race, T. H. Chiu, and R. L. Lum, *App. Surf. Sci.* 157, 132 (2000)). A copy of the publication is in the Appendix section of this report.

## **4 Impact**

### **4.1 Student Impact**

Eleven students were involved with this project. Ten of the students were African American including seven women. Thomas Weldeghiorghis, a graduate student in physical chemistry, was interested in using the secondary ion mass spectrometer to measure the In diffusion profiles for various stoichiometries as part of his thesis requirement. Weldeghiorghis transferred to Washington University at the end of his first year for personal reasons. Andrea Greene, an undergraduate physics student at Spelman College, took over the work of Weldeghiorghis and a scientific publication resulted from her effort. Shevon Johnson, an undergraduate transfer student from Spelman, joined the project in September 1998 and is being trained to operate the MBE reactor. Ms. Johnson is currently completing a summer internship with TLC Precision Wafer Manufacturing. These students have or are developing critical skills in vacuum techniques and surface

analysis. Jason Collins, an undergraduate physics student became proficient in the operation and use of the electron microscope. Collins completed his studies for the BS degree in Physics in December 1998 and is currently enrolled at RPI in the MS program in mechanical engineering and information technology. Greene recently completed the Dual Degree Program with a BS in physics from Spelman College and a BS in mechanical engineering from Georgia Tech.

Five other undergraduate students and three graduate students have worked in the laboratory on a rotational basis for one or two semesters. These students sought to have a good lab experience and received support as funds were available. The ready availability of funds was a serious issue that affected the recruitment of potential research students and the productivity of all the students involved in the project.

#### **4.2 Institutional Impact**

This FAR grant has enabled the MBE facility here at Clark Atlanta to achieve operational status. The FAR grant has also leveraged the award of grants from NSF, DOE, Corning, Inc., and from the Lawrence Livermore National Laboratory. Strong ties have been established and maintained with researchers at Duke University, North Carolina State University, Georgia State University, JPL, NASA-Lewis, Lucent Technologies, Lasertron and TLC Precision Wafer Manufacturing.

#### **4.3 Faculty Impact**

Several talks on this subject matter have been presented (see Appendix). Invited talks at student research seminars were given at Clark Atlanta University, Spelman College and Morehouse College. These schools are all HBCU's located in Atlanta, Ga. Invited talks at professional research seminars and conferences were given at Lasertron, Inc, the Jet Propulsion Laboratory and at the 20th Annual Conference of the National Society of Black Physicists. An invited talk and a student poster presentation were given at the Fifth (1998) NASA HBCU's Conference. The PI also moderated discussion sessions at the 11th and 12th Annual Conferences on the National Conference of Black Physics Students where he had the opportunity to discuss his work and interests. The PI has acquired tenure at the University during the period of this award.

#### **4.4 Project Difficulties**

The timeliness of the supplemental awards is a critical issue that the needs to be addressed. In the case of this project, the effective dates for the second year supplement was January 14, 1998 to September 24, 1998. These funds were not released, however, until February 19, 1998. Consequently the supported period for the second year effort was only eight (8) months. The unsupported lapse between the end of the first year period of the project on September 24, 1997 and the arrival of the second year's supplement was four (4) months. Likewise, the effective dates for the third year supplement was January 14, 1999 to September 24, 1999 with an actual release date of February 8, 1999. The supported period for the third year was again only eight (8) months with a four (4) month lapse from the end date of the second year. A substantial portion of this grant was allocated to student support in the form of stipends and tuition. Funds for these activities

and others related to the project cannot be disbursed until the University has received authorization from NASA - FAR. A strong effort should be made to ensure that supplements arrive on schedule. Dr. Samuel Alterovitz, the technical monitor for this project, is to be commended for his efforts in expediting this matter on the project's behalf. The effective dates of the supplements should also be contiguous with the prior year period.

## 5.0 Appendix

### 5.1 Talks

1. M. D. Williams-"Overview of Center of Excellence in Microelectronics and Photonics", Honors Seminar, Department of Chemistry, Morehouse College, Atlanta, GA, 4/24/96 (Invited).
2. M. D. Williams-"Physics of Free Standing Quantum Wells", Fall Meeting of the Southeastern Section of the American Physical Society, Decatur, GA, 11/14-16/96 (Contributed).
3. M. D. Williams-"Overview of Center of Excellence in Microelectronics and Photonics", Seminar, Department of Physics, Spelman College, Atlanta, GA, 2/11/97 (Invited).
4. M. D. Williams-Graduate Breakout Session (Co-Moderator): "Getting Through Qualifiers, Choosing an Advisor, Starting Research/Deciding on a Project, Applying for Postdocs/Industry?Academia, Dealing with Department Politics", 11th Annual National Conference of Black Physics Students, Massachusetts Institute of Technology, Cambridge, MA 2/27-3/2/97 (Invited).
5. M. D. Williams-"In Segregation at the Growth Front of the GaAs/In<sub>0.30</sub>Ga<sub>0.70</sub>As (100) Heterojunction", Seminar, Lasertron, Inc., Bedford, MA 2/28/97 (Invited).

6. M. D. Williams-"In Segregation at the Growth Front of the GaAs/In<sub>0.30</sub>Ga<sub>0.70</sub>As (100) Heterojunction", Device Research and Applications Section Seminar, Jet Propulsion Laboratory, Pasadena, CA, 3/12-13/97 (Invited).
7. M. D. Williams-"Materials Issues in III-V Compound Semiconductors", 20th Annual Meeting of the National Society of Black Physicists, Lawrence Berkeley National Laboratory, Berkeley, CA 3/27-29/97 (Invited).
8. A. L. Greene and K. A. Goodman -"Secondary Ion Mass Spectrometry of InGaAs/InP (100) Multiple Layer Semiconductors", Seminar, Department of Physics, Clark Atlanta University, Atlanta, GA, 4/1/98 (Contributed).
9. M. D. Williams-"Growth and Characterization of III-V Semiconductors for Device Applications", NASA HBCUs Research Conference, Ohio Aerospace Institute, Cleveland, OH, 4/8-9/98 (Invited).
10. J. H. Collins-"Growth and Characterization of III-V Semiconductors for Device Applications", NASA HBCUs Research Conference, Ohio Aerospace Institute, Cleveland, OH, 4/8-9/98 (Contributed).
11. J. Collins - "Free Standing Quantum Wells", Annual Student Scientific Research Symposium, Dept. of Biological Sciences, Clark Atlanta University, Atlanta, GA, 4/30/98 (Contributed).

12. A. L. Greene - "Secondary Ion Mass Spectrometry of InGaAs Semiconductors Grown by Chemical Beam Epitaxy", Annual Student Scientific Research Symposium, Dept. of Biological Sciences, Clark Atlanta University, Atlanta, GA, 4/30/98 (Contributed).
13. M. D. Williams - "Growth and Characterization of III-V Semiconductors for Device Applications", Program in Physical Sciences seminar, Spelman College, Atlanta, Ga., 7/19/99 (Invited).
14. M. D. Williams-Graduate Breakout Session (Co-Moderator): "Expectations of Graduate School" and "The End is Near, Now What? The Job Market". 14th Annual National Conference of Black Physics Students, North Carolina A & T State University, Greensboro, NC., 3/16-19/00 (Invited).

## **5.2 Un-Refereed Publications/Abstracts:**

1. Growth and Characterization of III-V Semiconductors for Device Applications, M. D. Williams, Research and Technology Report 1996, Office of Equal Opportunity Programs, Minority University Research and Education Division, National Aeronautics and Space Administration, 74 (1997).

2. "Materials Issues in III-V Compound Semiconductors", M. D. Williams, Proc. 20th Annual Meeting of the National Society of Black Physicists, (1998).
3. M. D. Williams-"Growth and Characterization of III-V Semiconductors for Device Applications", M. D. Williams and J. H. Collins, NASA HBCUs Research Conference Agenda and Abstracts, National Aeronautics and Space Administration, Ohio Aerospace Institute, 12 (April 1998).
4. J. Collins- "Free Standing Quantum Wells", J. Collins, M. D. Williams, and H. W. H. Lee, Clark Atlanta University Department of Biological Sciences Annual Student Scientific Research Symposium, Atlanta, GA (April 1998).
- 2.0 A. L. Greene - "Secondary Ion Mass Spectrometry of InGaAs Semiconductors Grown by Chemical Beam Epitaxy", A. L. Greene and M. D. Williams, Clark Atlanta University Department of Biological Sciences Annual Student Scientific Research Symposium, Atlanta, GA (April 1998).

### **5.3 Refereed Publications (Attached):**

"Comparison of InGaAs (100) Grown by Chemical Beam Epitaxy and Metal Organic Chemical Vapor Deposition", M. D. Williams, A. L. Greene, T. Daniels-Race, T. H. Chiu, and R. L. Lum, *App. Surf. Sci.* 157, 132 (2000).